

Diffusion of linear and branched alkanes in ZSM-5. A quasi-elastic neutron scattering study

H. Jobic*

Institut de Recherches sur la Catalyse, CNRS, 2 av. Albert Einstein, 69626 Villeurbanne Cedex, France

Abstract

The diffusivities of long *n*-alkanes in ZSM-5 have been measured by quasi-elastic neutron scattering (QENS). Self-diffusion coefficients and activation energies for chains up to C₁₄ have been obtained. Reasonable agreement is observed with single-crystal membrane experiments, except for C₆, but large discrepancies are found with the zero-length column (ZLC) method. The diffusivities predicted by a hierarchical simulation diverge from those measured by QENS after C₆, although the activation energies for diffusion are comparable. The discrepancy with MD simulations is larger. QENS results show that diffusion of branched alkanes is much more restricted than the one of linear alkanes in this structure. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolites, which are crystallised microporous materials, are widely used for different applications such as catalysis or separation of gases and hydrocarbons. In particular, MFI-type zeolites (ZSM-5 and its purely siliceous form: silicalite) have found several applications in shape-selective catalysis, in the field of refining, and in adsorption processes. Zeolitic membranes, i.e. membranes where the zeolite is either deposited on or synthesised inside a ceramic support, are mainly based on the MFI structure. Since the channels of this structure have free apertures about 5.5 Å in diameter, a straightforward application of this type of mate-

rial would be the separation of alkane isomers. The minimum kinetic diameter of linear alkanes is of 4.3 Å, while the one of small branched alkanes varies between 5.0 and 6.2 Å. These values should only be viewed as qualitative indications. In fact, the channels diameters reported in the Atlas of Zeolite Structure Types [1] are based on an arbitrary value of 1.35 Å for the oxygen radius whereas values ranging from 1.0 to 1.6 Å have been suggested in the literature [2]. Furthermore, the concept of kinetic diameter implies a spherical representation of a molecule, which is an oversimplification, as well as for the supposed rigidity of the molecule or of the framework.

Therefore, there is no quantitative theory at the present time which is able to predict the diffusivities of linear or branched alkanes, because there will be a strong dependence on the

* Tel.: +33-4-724-453-01; fax: +33-4-724-453-99.

E-mail address: jobic@catalyse.univ-lyon1.fr (H. Jobic).

size and shape of the molecule with respect to the zeolite pores. Experimental or simulation methods have to be used. However, there are still puzzling differences between the values of the diffusion coefficients obtained by various experimental and theoretical techniques. In the case of linear alkanes in the MFI structure, differences of up to six orders of magnitude have been reported [3]. For short alkanes (up to C_6), quasi-elastic neutron scattering (QENS), pulsed-field gradient NMR (PFG NMR) and molecular dynamics (MD) simulations are in reasonable agreement, but large deviations are noted with other methods like chromatography, frequency response, and single-crystal membrane (see Ref. [4] for a recent review).

Linear alkanes longer than C_6 have been much less studied, both experimentally and theoretically. In particular, no microscopic diffusivities were available when simulation studies were performed for chains as long as C_{20} [5,6]. Simulations were ahead of experiment for such systems. The first simulation study was based on a hierarchical method [5] and the second one was a MD simulation [6]. Large differences can be noticed between the two simulations. The first one predicts a gradual decrease of the self-diffusivity up until C_4 , with a small plateau from C_4 to C_8 , a decrease for C_{10} and then almost a constant diffusivity up to C_{20} [5]. Activation energies for diffusion are small, ≈ 5 kJ/mol, for chains up to C_8 , and increase to about 12 kJ/mol for longer chains [5]. The MD method yields large diffusivities, ranging between 10^{-4} and 10^{-5} cm^2/s for C_4 up to C_{20} , with higher self-diffusivities for C_8 and C_{16} [6]. Although this ‘resonant effect’ was found to be more pronounced at low temperature and infinite dilution, oscillations are still expected at 300 K at small loading, after averaging the self-diffusivity tensor. Apparent negative activation energies are calculated for certain chain lengths, such as C_8 , C_9 and C_{10} . Such predictions are worth testing experimentally.

Very recently, the rotational and translational dynamics of *n*-octane in ZSM-5 were studied

using a combination of ^2H NMR and QENS techniques [7]. It was found that, for a loading of about 2 molecules per unit cell, the *n*-octane molecules were essentially located in the straight channels. One-dimensional (1D) diffusion was derived from QENS measurements, the averaged self-diffusion coefficient being one or two orders of magnitude lower than in the simulations, performed at infinite dilution. In view of this large discrepancy, it seemed necessary to study the loading dependence of the self-diffusivity of this molecule. Furthermore, the diffusivity of longer alkanes is now accessible by new QENS spectrometers.

Much less work has been performed on the diffusion behaviour of branched alkanes in the MFI structure. PFG NMR measurements are not possible because of short T_2 values [8]. The first MD simulations, using the united atom potential, are only approximate [9]. A slow diffusivity has been recently found by QENS for isobutane in ZSM-5, in agreement with supported membrane results [10].

In this paper, self-diffusion coefficients and activation energies of linear alkanes in ZSM-5 are reported. Chain lengths up to C_{14} are considered. The QENS results are compared with those obtained from techniques (experimental and simulations) which are able to study a wide series of *n*-alkanes. Relative diffusivities of linear and branched alkanes in this zeolite are discussed.

2. Theory

For hydrogenous molecules, like alkanes, the incoherent scattering from hydrogen dominates because of the relatively larger incoherent cross-section of this atom. In the energy domain studied in this work, ± 12 μeV , the scattered intensity can be analysed simply in terms of the incoherent translational scattering function, because vibrational and rotational motions involve larger energy transfers. Self-diffusion coefficients can be obtained from the incoherent

translational scattering function since it gives information on the long-range diffusion of individual molecules. When the scattering is coherent, collective motions are probed [11].

The incoherent translational scattering function for a molecule following Fick's law or jump diffusion is a Lorentzian function:

$$S(Q, \omega) = \frac{1}{\pi} \frac{\Delta \omega(Q)}{\omega^2 + (\Delta \omega(Q))^2} \quad (1)$$

where $\hbar Q$ describes the neutron momentum transfer and $\hbar \omega$ is the neutron energy transfer. For isotropic diffusion, if the momentum transfer is sufficiently small, i.e. when one is looking at the diffusion over large distances, the half-width at half-maximum (HWHM) of the Lorentzian is DQ^2 , where D is the self-diffusion coefficient. A plot of the HWHM as a function of Q^2 should be a straight line. At larger momentum transfers, the HWHM deviates from a straight line because the system cannot be considered anymore as continuous, this deviation is characteristic of a jump diffusion. The jump diffusion models are based on the following hypotheses: the molecule remains on a given site during a time τ . After this time, it jumps to another site, the time taken for the jump being much shorter than the residence time.

In some systems, for example *n*-pentane in NaX [12], the jump length is a constant. For *n*-alkanes in ZSM-5, the jump length distribution of Singwi and Sjölander [13] was found to fit the data correctly [14,15]. For an isotropic diffusion, the HWHM of this model is given by:

$$\Delta \omega(Q) = \frac{1}{6\tau} \frac{Q^2 \langle r^2 \rangle}{1 + Q^2 \langle r^2 \rangle / 6} \quad (2)$$

where $\langle r^2 \rangle$ is the mean-square jump distance. This quantity and the mean residence time τ can be determined from refinements of the spectra. A self-diffusion coefficient can then be

obtained from Einstein's equation in three dimensions:

$$D = \frac{\langle r^2 \rangle}{6\tau} \quad (3)$$

At small Q values, corresponding to distances of about 60 Å, the HWHM of the jump diffusion model, Eq. (2), reduces to DQ^2 , using Eq. (3). This corresponds to Fickian diffusion. It means that, when looking at the diffusion over a few unit cells, the self-diffusion coefficient can be derived independently of any model.

In the MFI structure, the diffusion is anisotropic so that the self-diffusion coefficient becomes a tensor. Previous simulations have shown that, for small *n*-alkanes concentrations, the diffusion is larger along the straight channel which runs along the *y*-axis, than along the zigzag channel which runs along the *x*-axis [5,6]. The mobility along the *z*-direction is even much smaller since the molecule has to migrate alternatively along the two other directions. One can characterise diffusion along the straight channels with D_{\parallel} and along the zigzag channels with D_{\perp} . The incoherent translational scattering function in such a geometry was derived for liquid crystals [16]. If θ defines the angle between Q and the *y*-direction, the scattering function, after powder averaging is:

$$\begin{aligned} S(Q, \omega) &= \frac{1}{2\pi} \int_0^{\pi} \frac{(D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta) Q^2}{\omega^2 + (D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta)^2 Q^4} \\ &\quad \times \sin \theta d\theta \end{aligned} \quad (4)$$

For each spectrum, i.e. for each Q value, the ratio D_{\parallel}/D_{\perp} can be directly fitted to the QENS intensities.

When the diffusion is 1D, the spectra obtained at different Q values can be refined simultaneously with the jump diffusion model

of Singwi and Sjölander. The HWHM of this model, in a given direction, can be written as:

$$\Delta\omega(Q) = \frac{D_{\parallel} Q^2 \cos^2 \theta}{1 + D_{\parallel} Q^2 \cos^2 \theta \tau} \quad (5)$$

The theoretical profile is obtained after substituting Eq. (5) in Eq. (1), and taking the powder average.

3. Experimental

The QENS experiments were performed on the backscattering spectrometer IN16, at the Institut Laue–Langevin in Grenoble, France. Unpolished Si(111) crystals were used as analysers, the energy transfer being analysed in a window of $\pm 12 \mu\text{eV}$. The energy resolution, which was measured with a vanadium tube, has a Gaussian line shape with a HWHM of about $0.45 \mu\text{eV}$. The accessible time scale on this spectrometer is in the range 0.2–10 ns. The momentum transfer resolution is worse than on a time-of-flight spectrometer, due to geometrical reasons, so that it is more difficult to avoid completely the Bragg peaks of the zeolite. Recording times were about 10 h for each run.

The ZSM-5 sample was the same as in previous studies on alkanes diffusion [14,15]. The Si/Al ratio is of about 35 and the equivalent radius of the crystals is $\approx 15 \mu\text{m}$. The zeolite is activated by heating to 770 K in a glass reaction vessel and pumped to 10^{-4} Pa at the same temperature. After cooling, *n*-alkanes were adsorbed onto the pretreated zeolite. Three loadings of *n*-octane were studied: 0.9, 2.2 and 5 molecules per unit cell. The thickness of the zeolite powder was selected to give a transmission of 90%. For longer chains, C₁₀, C₁₂, and C₁₄, the loading was chosen so that the scattering was similar to the intermediate concentration of *n*-octane, i.e. there were about 39 hydrogen atoms per unit cell. This corresponds to 1.8 *n*-decane, 1.5 *n*-dodecane, and 1.3 *n*-tetradecane per unit cell. The samples were transferred in-

side a glovebox into cylindrical aluminum containers of annular geometry. Cells containing different amounts of dehydrated zeolite were also prepared. Their signal was subtracted from the spectra recorded with the samples containing the alkanes, for the same zeolite powder thickness.

4. Results and discussion

For *n*-octane at low loadings and for the longer chains, refinements of the spectra individually with Eq. (4), after convolution with the instrumental resolution, yielded large values for the ratio D_{\parallel}/D_{\perp} . Simultaneous fits to all spectra could then be made using the 1D jump diffusion model (Eqs. 1 and 5). This model gave good fits to all spectra, which is illustrated in Fig. 1(a) for one scattering angle.

The self-diffusion coefficients were obtained in two different ways: (i) from the small Q range where the system follows Fickian behaviour, and (ii) from the parameters of the jump model, $\langle r^2 \rangle$ and τ , using Einstein's equation in one dimension. Due to the difficulty in resolving Bragg peaks, the determination of the two parameters of the jump model is less precise than on a time-of-flight instrument [14].

At the largest *n*-octane loading, the anisotropy was negligible at low Q values so that spectra could be fitted with an isotropic diffusion (see Fig. 1(b)). However, some anisotropy was still found at large Q values, corresponding to distances of the order of the length of the channels. This suggests that the molecules are mainly confined in the channels.

For all *n*-alkanes at the different temperatures, the mean jump distance is in the range 3–10 Å, and the residence time varies from 7.0×10^{-9} to 6.0×10^{-10} s. The averaged diffusivities obtained for *n*-octane at the various loadings are reported in Table 1. The value obtained at 300 K for the intermediate loading has already been published [7]. The estimated errors vary between 50% and a factor 2, de-

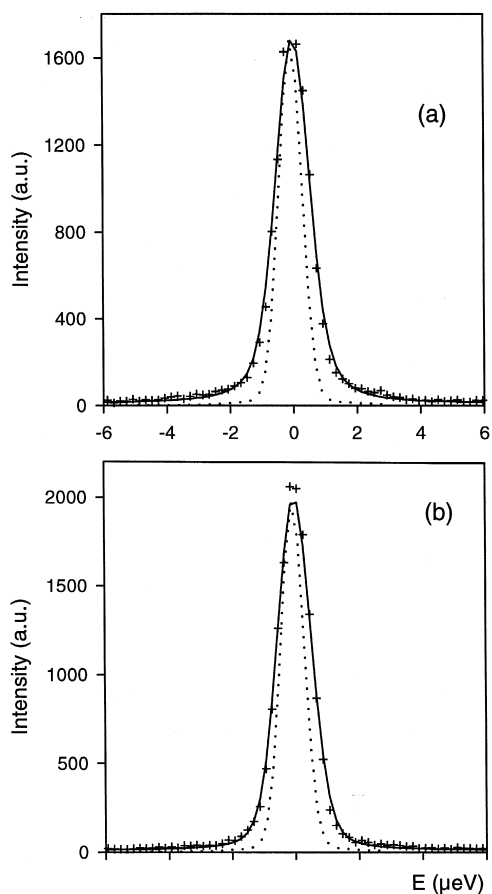


Fig. 1. Comparison between experimental (+) and calculated (full line) QENS spectra for two loadings of *n*-octane in ZSM-5 at 300 K ($Q = 0.29 \text{ \AA}^{-1}$): (a) 0.9 molecule per unit cell, (b) 5 molecules per unit cell. The dotted line represents the resolution function.

pending on the statistics. For 1D diffusion, the averaged self-diffusion coefficient is simply $1/3D_{\parallel}$.

It is surprising that the loading dependence of the *n*-octane diffusivity is rather small. By increasing the loading from 0.9 to 5.0 molecules per unit cell, the diffusion coefficient decreases

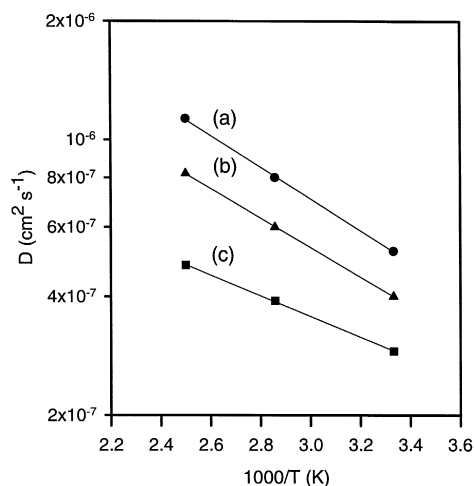


Fig. 2. Arrhenius plot for the self-diffusion coefficients of *n*-octane in ZSM-5, as a function of loading: (a) 0.9 molecule per unit cell, (b) 2.2 molecules per unit cell, and (c) 5 molecules per unit cell.

only by a factor of 2 (Table 1). This is illustrated by the small difference in broadening between Fig. 1(a) and (b). Such a loading behaviour is in agreement with previous MD simulations which predicted a decrease by less than one order of magnitude between low and high loadings of *n*-hexane [17,18]. However, the more recent MD simulation predicts a decrease by two orders of magnitude for the diffusivity of *n*-octane at 300 K, when increasing the loading from 0.5 to 4 molecules per unit cell [6]. This is in disagreement with the QENS results.

The self-diffusion coefficients for *n*-octane, obtained at the three loadings, are plotted in Fig. 2 versus inverse temperature. The obtained activation energies are listed in Table 1. The value determined at low loading, 7.7 kJ/mol, is not much different from the one derived from the hierarchical method, 4.3 kJ/mol [5]. The appar-

Table 1

Averaged self-diffusion coefficients and activation energies for *n*-octane in ZSM-5 at different loadings

	$D_{(300 \text{ K})} (\text{cm}^2/\text{s})$	$D_{(350 \text{ K})} (\text{cm}^2/\text{s})$	$D_{(400 \text{ K})} (\text{cm}^2/\text{s})$	$E_a (\text{kJ/mol})$
0.9 molecule/unit cell	5.2×10^{-7}	8.0×10^{-7}	1.13×10^{-6}	7.7
2.2 molecules/unit cell	4.0×10^{-7}	6.0×10^{-7}	8.2×10^{-7}	7.2
5.0 molecules/unit cell	2.9×10^{-7}	3.9×10^{-7}	4.8×10^{-7}	5.0

ent negative value computed from MD simulations [6] is not found by experiment.

For longer *n*-alkanes, the 1D jump diffusion model gave best fits to the experimental spectra. However, at small Q values, broadenings of the elastic peak are less than the instrumental resolution so that an isotropic diffusion model can also be used, it yields only slightly larger weighted profile R factors [19]. The diffusivity of long chains decreases steadily with increasing number of carbon atoms (Table 2). The self-diffusion coefficients obtained by QENS at 300 K for low loadings are plotted in Fig. 3. Results obtained previously for shorter chains [14,15] are also included. The QENS diffusivities are compared with those obtained from techniques which were able to study a wide series of *n*-alkanes. For example, PFG NMR data which are in good agreement with QENS for short alkanes (up to C_6) are not included. It appears from Fig. 3 that the very large and almost constant diffusivities predicted by the MD simulations [6] are not observed by QENS. Reasons usually proposed to explain the larger theoretical diffusivities such as perfect crystal, infinite dilution, and rigid framework, seem insufficient to account for this large discrepancy. It is probable that the united atom model is too simple for alkanes longer than C_4 . The trend found by the hierarchical simulation approach [5] is in better agreement with QENS, although the two sets of data start diverging for C_6 . The step measured by QENS between C_6 and C_8 seems to be shifted in the hierarchical simulation between C_8 and C_{10} .

The comparison with the single-crystal membrane results is interesting: a good agreement is observed for short chains and for C_8 , but a big gap is noticeable in between. Even if the mem-

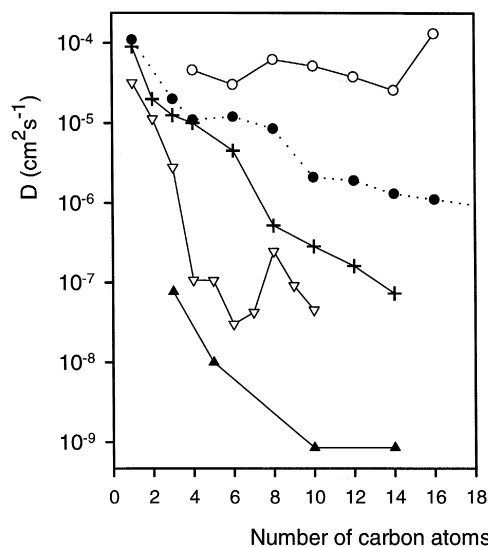


Fig. 3. Diffusion coefficients obtained at 300 K by different techniques, for *n*-alkanes in the MFI structure: (○) MD simulations [6], (●) hierarchical simulation [5], (+) QENS, (▽) single-crystal membrane [4], and (▲) ZLC [20].

brane configuration only measures diffusivity in one direction, it is difficult to understand these large variations. The ZLC diffusivities are two or three orders of magnitude lower than the QENS values. The number of points measured by ZLC is not sufficient to ascertain that the trend observed by this technique is similar to the QENS or hierarchical simulation results.

It can be noted in Fig. 3 that all the diffusivities seem to converge for small alkanes: the data are contained within one order of magnitude for C_1 and C_2 . However, discrepancies become larger when the number of carbon atoms increases: for the long chains, the values are scattered over five orders of magnitude.

Activation energies for diffusion, determined by the different methods discussed above, are plotted in Fig. 4 as a function of carbon number.

Table 2

Averaged self-diffusion coefficients and activation energies for long *n*-alkanes in ZSM-5

	$D_{(300\text{ K})}$ (cm^2/s)	$D_{(350\text{ K})}$ (cm^2/s)	$D_{(400\text{ K})}$ (cm^2/s)	$D_{(460\text{ K})}$ (cm^2/s)	E_a (kJ/mol)
<i>n</i> -decane	2.8×10^{-7}	4.9×10^{-7}	7.9×10^{-7}		10.3
<i>n</i> -dodecane	1.6×10^{-7}	3.0×10^{-7}	5.0×10^{-7}		11.4
<i>n</i> -tetradecane		1.5×10^{-7}	2.25×10^{-7}	4.0×10^{-7}	11.9

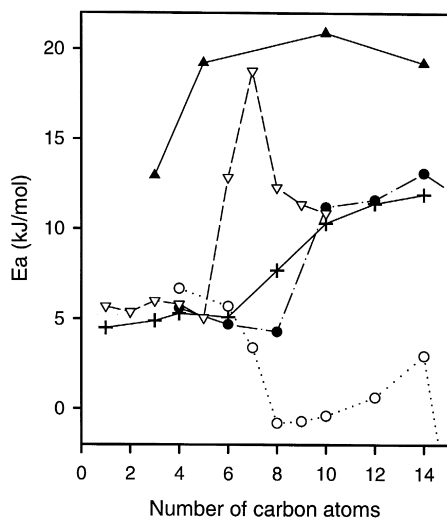


Fig. 4. Activation energies for diffusion determined for *n*-alkanes in the MFI structure, by different techniques: (○) MD simulations [6], (●) hierarchical simulation [5], (+) QENS, (▽) single-crystal membrane [4], and (▲) ZLC [20].

Most of the experimental and theoretical techniques indicate small activation energies for short alkanes, about 5 kJ/mol. For chains longer than C₆, the QENS data are in reasonable agreement with the hierarchical approach, except for C₈ where the value obtained in the simulation is 50% smaller. The apparent negative activation energies predicted by the MD simulations are not observed. Good agreement is found with the results measured by the single-crystal membrane technique for small alkanes (up to C₄) and for C₁₀, but a difference has to be stated for C₆ and to a lesser extent for C₈. The values reported by the ZLC method are much larger, measurements with methane and ethane with this technique would be useful, if feasible.

The diffusivities of branched alkanes in ZSM-5 are more difficult to determine by QENS, because they are much smaller than the corresponding linear alkanes. In fact, the diffusion of isobutane and of *n*-butane cannot be measured on the same QENS spectrometer, because they occur on different time scales. A spectrum obtained for isobutane at 570 K is shown in Fig. 5(a). It is clear that the broadening of the elastic peak, which is related to the long-range mobil-

ity, is very small for isobutane compared to *n*-octane at an even lower temperature of 400 K (Fig. 5(b)). The self-diffusion coefficient obtained by QENS for isobutane at 570 K is 5.5×10^{-8} cm²/s [10]. Extrapolation to room temperature, using an activation energy of 17 kJ/mol [10], indicates that the diffusivity of isobutane is more than three orders of magnitude lower compared with *n*-butane. Preliminary measurements show that the diffusion coefficient of 3-methylpentane is lower by about a factor 5 when compared with isobutane. This is in reasonable agreement with the supported membrane technique, which yields a diffusivity of 4.0×10^{-8} cm²/s for 3-methylpentane at 523 K [21].

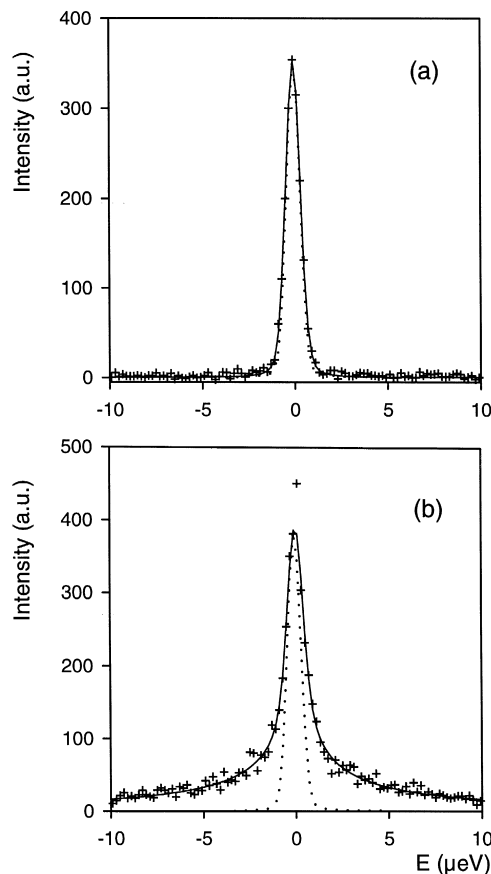


Fig. 5. Comparison of the broadenings obtained for a branched and a linear alkane in ZSM-5: (a) 3 isobutane per unit cell at 570 K, (b) 2.2 *n*-octane per unit cell at 400 K ($Q = 0.87 \text{ \AA}^{-1}$). The dotted line represents the resolution function.

5. Conclusions

Very few experimental techniques are able to measure the diffusivities of both short and long *n*-alkanes in the MFI structure. This is possible with the QENS method. The diffusion coefficients which have been derived are in agreement with single-crystal membrane experiments for short chains and for C₈, but the dip measured by this technique in between is not observed by QENS. The diffusion coefficients determined by the ZLC technique are more than two orders of magnitude lower.

In previous studies, it was noticed that the agreement between QENS values and simulations was excellent for short *n*-alkanes. In this work, the discrepancy, which is found for longer *n*-alkanes and for isobutane, should motivate more simulations. New codes are available which will allow simulations considering a flexible framework for the zeolite with full atomistic model for the adsorbates.

In this zeolite, QENS measurements indicate clearly that branched alkanes diffuse much more slowly than linear alkanes, at the microscopic level. Permeability measurements with silicalite membranes give a *n*-butane/isobutane permselectivity of 60, at 450 K [21]. More recent experiments yield even higher permselectivities, about 1000 for similar coverages [22], which is more in line with what one can expect from the diffusion coefficients measured by QENS.

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